Effects of smelter pollutants on forest leaf litter decomposition near a nickel–copper smelter at Sudbury, Ontario

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Forest soils and litter in the vicinity of a large nickel–copper smelter at Sudbury, Ont. are known to be contaminated with a variety of heavy metals. In view of this, studies were carried out to determine if forest litter decomposition processes have been affected. The effects of nickel and copper on the decomposition of forest litter were investigated using a variety of techniques in which contaminated and control sites were compared. At contaminated sites an increase in litter standing crop was found. This was related to lower rates of litter decomposition at these sites, as evidenced by reduced rates of breakdown of litter in mesh bags, compared with uncontaminated sites. Lower rates of CO_2 flux and acid phosphatase activity were also found at the contaminated sites. In a laboratory experiment, the addition of copper and (or) nickel to a homogenate of leaf litter was shown to depress the rate of dry weight loss and CO_2 flux. Negative effects commenced at metal concentrations comparable to those observed in litter at contaminated sites in the field.

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Les sols forestiers et la litière des sols au voisinage d'un haut fourneau de cuivre et de nickel à Sudbury, en Ontario, sont contaminés par plusieurs métaux lourds. On a donc poursuivi des études pour déterminer si cette pollution affecte les processus de décomposition de la litière des sols forestiers. Les effets du nickel et du cuivre sur la décomposition de la litière ont été étudiés par plusieurs méthodes permettant de comparer sites contaminés et sites témoins. Dans les sites contaminés, on constate une augmentation de la biomasse de la litière. Cette augmentation est reliée à des taux plus faibles de décomposition de la litière dans ces sites que dans les site non contaminés, ainsi que le démontrent les taux réduits de décomposition de la litière dans des sacs maillés. Une expérience en laboratoire montre que l'addition de cuivre et (ou) de nickel à un homogénat de litière de feuilles diminue le taux de perte en poids sec et le flux de CO_2. Ces effets négatifs débutent lorsque les métaux ont une concentration comparable à celle que l'on observe dans la litière des sites contaminés.

[Traduit par le journal]

Introduction

Previous studies in the Sudbury area have shown that forest communities have been severely affected by a number of interacting factors, including logging, fire, and smelter fumigations. Ground-level fumigations from numerous roast beds (pre-1928) were especially devastating. Emissions from smelter facilities constructed as early as 1913 (located at Copper Cliff, Coniston, and Falconbridge) have also been considerable, and have contributed to contamination of aquatic and terrestrial ecosystems close to the Sudbury smelters. The major pollutants have been sulfur dioxide, sulfuric acid mists, and heavy metals such as nickel, copper, iron, and cobalt (for example, see Hutchinson and Whitby 1977; Freedman and Hutchinson 1979, 1980*a*, 1980*b*). The soils are acidic and acid rains have had limited effect in increasing their acidity.

In view of the marked toxicity of many heavy metals to microorganisms and to litter decomposition processes (Jordan and Lechevalier 1975; Tyler 1975*a*, 1975*b*; Watson *et al.* 1976; Strojan 1978*a*), it was postulated that the contamination of Sudbury area soils was sufficient to affect rates of litter breakdown in contaminated forested communities close to the smelters. Appreciable litter accumulation would have profound implications, suggesting a major reduction in nutrient cycling in the contaminated areas. The present studies compared contaminated sites close to the largest Sudbury smelter, at Copper Cliff, with uncontaminated control sites. The studies included (*i*) measurement of litter standing crop relative to rates of litter input; (*ii*) estimation of populations of fungi and ar-

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thropods in litter; and (*iii*) determination of activity indices related to rates of litter breakdown, including (*a*) rates of decomposition of litter in litterbags placed at contaminated and control sites; (*b*) the relative rates of decomposition of foliage collected from contaminated versus control sites; and (*c*) CO_2 flux and enzyme activity of forest soils. Studies were also made of the effects of heavy metal additions to a litter homogenate on the subsequent rates of litter decomposition following incubation in the laboratory.

Materials and methods

Leaf litter standing crop

Standing litter was collected at nine forested stands at distances ranging from 3.5 to 34.3 km from the Copper Cliff smelter in May 1976. Litter was sampled by randomly placing fifteen 0.25 m × 0.25 m quadrats per site, and hand-sorting material in the field into "litter" and "duff." These were defined as "litter" (01, leaves recognizable to tree species) and "duff" (02, recognizable as leaf fragments, as opposed to amorphous organic matter, or humus) after Daubenmire (1974). Leaf litter only was collected, with twigs, cones, etc. being excluded. The material was dried at 105°C, weighed, and the dry weight of litter and duff per unit ground area was calculated.

Litter accumulation ratio

Litter accumulation was estimated using the ratio of litter standing crop to litter fall. In this study, litter standing crop was estimated by litter plus duff, as defined in the previous section. Leaf litter fall was estimated for four forested stands (two contaminated sites and two control sites) by exposing six randomly placed litter traps per site for a collection period of 1 year (May 1976 to May 1977). The litter traps were constructed of square wooden frames (1.3-cm-thick plywood) with internal dimensions of 1 m × 1 m, a height of 20 cm, and supported by legs 20 cm above the ground surface (after Newbould 1967; Medwecka-Kornas 1971). The bottoms of these frames were made of tightly stretched fiber glass screening (15 mesh, 0.17 cm screen size). Litter was collected from the traps at monthly intervals during the snow-free season, but only a single collection was made following the winter period of continuous snow cover. The input of leaf litter from the herbaceous ground flora was not included in this sampling method. It was determined separately in early autumn of 1976 by harvesting the standing crop of herbaceous leaf material in six 1 m × 1 m quadrats per site.

Litterbag leaf decomposition and cation loss

Rates of leaf decomposition were studied by exposing litter contained in inert mesh bags in natural habitats (Bocock *et al.* 1960; MacFadyen 1971; Jensen 1974; Millar 1974). In this study, 20 cm × 13 cm envelopes were constructed from fiber glass screening (15 mesh, 0.17 cm screen size), and filled with known weights of leaves of three tree species (*Betula papyrifera*, *Populus tremuloides*, and *Pinus strobus*). These were collected as fresh leaf material from trees at uncontaminated forest sites in June 1976. Bundles of *P. strobus* needles were made by tying the needles together with nylon thread, and these were placed into the litterbags. The *P. tremuloides* and *B. papyrifera* leaves, minus the petiole, were put loosely into the litterbags. Initial ovendry weights of the materials were calculated from known air-dry weights (8–16 days at room temperature) and the ratio of air-dry to ovendry (105°C) weights. The average weight of leaf tissue in these litterbags was ca. 4 gm dry weight.

The litterbags were placed on the soil surface at five forested sites (three contaminated and two control sites) on June 22, 1976. Collections of four or five replicates were made after intervals of 51, 117, 314, and 851 days. Collected materials were hand sorted to remove insects or obvious insect fecal material, after which ovendry weights were determined, and weight loss calculated.

The relative losses of basic cations (calcium, magnesium, and potassium) from leaves at various sites were determined by comparing initial amounts to those remaining after exposure in the field. The data are expressed as percent loss after the various exposure periods.

Decomposition of contaminated and control foliage

In this experiment, foliage of three tree species common in the Sudbury area (*Alnus rugosa*, *Acer rubrum*, and *Populus tremuloides*) was collected in September 1976 from one contaminated and two control forest sites. Litterbags were then prepared as previously described. These were placed on the forest floor at an uncontaminated forest site on May 1, 1977, and exposed for periods of 175 or 538 days, after which they were collected, and percent weight loss determined. Relative rates of weight loss were then correlated to foliar heavy metal (copper, nickel) concentrations.

Soil CO_2 evolution measurements

CO_2 flux was determined for soil samples collected from forest sites at various distances from the Copper Cliff smelter. Soil CO_2 flux was used as an index of soil respiration. It was determined by measuring (using a Beckman model 864 infrared gas analyzer) the rate of increase of CO_2 concentration in a closed, recirculating chamber system into which a soil sample had been deposited (MacFadyen 1971; Sestak *et al.* 1971). The rate of change in concentration, multiplied by the total system volume, yielded a volumetric rate of CO_2 evolution. This value can be standardized to soil fresh or dry weight, or to soil volume, if a standard core sample was analyzed. Details of the experimental apparatus used in the determinations are in Freedman (1978).

Soil samples for CO_2 flux determinations were collected in 1975 from mesic *Populus tremuloides* forest communities along a south-southeast transect centering on Copper Cliff, and in 1976 from mesic *P. tremuloides* forests, and from mesic mixed forest communities. Soil samples used in the above determinations were collected using standard aluminum cylindrical corers (internal diameter = 3.5 cm, height = 7.0 cm, volume = 269 cm^3). Twenty replicate cores per site were collected, but for the determinations the cores were pooled in groups of two, so that 10 determinations were made per site. All soil samples were allowed to equilibrate for 24 h inside a darkened growth chamber at 28°C before CO_2 flux was measured (also at 28°C).

In addition, in 1977, soil samples were collected from the 02-A1 soil horizon (duff-humus) of mesic mixed forest communities along a south-southeast transect, and these were analyzed for both CO_2 flux and acid phosphatase activity (see Soil acid phosphase activity).

For some soil samples, heavy metal concentrations were also analyzed, so that the relationship between soil heavy metal concentrations and soil CO_2 flux could be determined.

Soil acid phosphatase activity

Soil enzyme activity has been used as an index of soil metabolic processes in a number of studies (reviewed recently by Skujins 1976), including several recent studies on metal-polluted soils (Tyler 1974; Ebregt and Boldewign 1977; Juma and Tabatabai 1977).

The method used in this study to assay acid phosphatase activity was modified from Cox (1976). An extract of soil pro-

teins was made by shaking (using a wrist-action shaker) 25-g fresh weight of soil in 125 mL of a 2 *N* urea solution for 30 min (after Allen *et al.* 1974). This was followed by centrifugation to clear the extract. The activity of this extract was assayed by adding 0.2 mL of extract to 2.0 mL of 0.3 *M* potassium acetate (pH 5.5), and then incubating for 20 min at 24.0°C in a water bath in the presence of 0.2 mL of 36 m*M* *p*-nitrophenol phosphate substrate (initial substrate concentration = 3 m*M*). After 20 min, the acid phosphatase activity was stopped by adding 0.4 mL of 2 *N* sodium hydroxide to the reaction tube, and the yellow colour due to *p*-nitrophenol in the assay solution was determined at 410 nm using a Pye Unicam SP6-300 spectrophotometer. Concentration of *p*-nitrophenol was then determined from these absorbance readings from a standard curve prepared using various concentrations of *p*-nitrophenol. Blanks were run under identical conditions to determine any nonenzymic production of *p*-nitrophenol. Prior to the assay of soils from the Sudbury region, the enzyme activity assayed by the above method was confirmed by experiments which showed the effects of substrate concentration, enzyme concentration, and time of incubation (see Freedman 1978 for details of these preliminary experiments).

Ten replicate humus soil samples were collected from four forest stands south-southeast of Copper Cliff (two contaminated and two control sites) on April 29, 1977. These were assayed after 2 days equilibration at about 28°C in a darkened growth chamber, using the above method. On June 2, 1977, 10 replicate humus soil samples were collected from six forest sites (three contaminated and three control sites) and from mineral soil on an exposed hilltop close to the smelter, and the acid phosphatase activity was assayed 2 days after collection. The latter soil samples were also assayed for CO_2 flux, and had heavy metal concentrations determined.

Soil faunal collections

Soil fauna were collected by sampling with standard aluminum soil corers (volume = 269 cm^3) at four forest sites (two contaminated and two control sites) on July 14 and July 17, 1976. Sixty replicate cores were collected per site, and arthropods were extracted using a modified Berlese-Tullgren high gradient funnel system, with heat and chemical (naphthalene) repellent, over 2-day postcollection periods (after Hutchinson *et al.* 1974, 1976). Collected organisms were preserved in 90% ethanol. For purposes of classification, the arthropods were grouped as mites (Acarina), springtails (Collembola), and others (mostly Diptera, Coleoptera, and Hymenoptera).

Soil fungal populations

Soil fungal populations were estimated by the dilution plate count method (Black *et al.* 1965; Parkinson *et al.* 1971). Soil samples were collected from four forest sites (two contaminated and two control sites) using the cylindrical aluminum soil corers. Collections of four or five replicate cores were made on June 7, July 1, and July 8, 1976. Dilutions and plating were done the day after collection. The soil fungi were cultured on a Rose–Bengall agar (with streptomycin to inhibit bacteria), in 8.7-cm plastic petri plates (after Black *et al.* 1965). Plates were incubated at 27 ± 1°C for 8 days, and the number of fungal colonies were then counted. Identifications to genus of the commonly isolated colonies were made by Dr. J. Morgan-Jones of the Department of Botany, University of Toronto.

The metal tolerance of soil fungal populations was tested by adding copper, nickel, or both (as highly soluble chloride salts) to the nutrient agars, at concentrations ranging from 0 to 100 ppm of each metal. The relative numbers of colonies isolated in these treatments were compared with controls.

The effect of metal additions on litter decomposition

Litter used in this experiment was gathered from the 01 (litter) horizon in October 1976 at a control forest site 35 km south-southeast of the Copper Cliff smelter. This litter was supplemented with a 10% addition by weight of a homogenized garden compost litter, to increase biological activity. The litter was air dried, homogenized in a Waring blender, passed through a 5-mm sieve, and then thoroughly mixed. Analyses were made of pH, and total copper, nickel, iron, zinc, phosphorus, and nitrogen. Aliquots of 75 g air-dry litter (dry weight was calculated from sample air-dry: ovendry (105°C) weight ratios) were then placed in 2-L polyethylene containers, with perforated lids to allow atmospheric exchange. Enough copper chloride and (or) nickel chloride was added to give concentration ranges of from 70 to 10 000 ppm dry weight nickel, or 210 to 10 000 ppm dry weight copper. The lowest concentrations represent the initial levels of copper and nickel in the litter used in the experiment. They suggest that even at 34 km metal inputs from the smelter are above background, but they are sufficiently low to allow comparisons to be made with deliberate additions to 10 000 ppm.

The metals were added in an aqueous solution sufficient to bring the litter to 80% of its water holding capacity, and mixed in thoroughly. The various samples were then incubated in a darkened growth chamber at 28 ± 2°C. Water loss was determined gravimetrically every 2 or 3 days, and enough distilled water added to return the litter to 80% water holding capacity.

At the end of the experiment (60-day incubation period), the dry-weight loss was determined and expressed as a percentage of that of the control. The rate of CO_2 flux from aliquots of the litter was also determined at this time.

Chemical analyses

Total heavy metals or basic cations were determined on soil or plant samples previously dried (105°C for 24 h) and homogenized. Approximately 0.5 g of these samples was placed into 50-mL boiling tubes. These were first predigested at room temperature in 6-mL of a 5:2 (v:v) nitric – perchloric acid mixture for 24 h, and then digested at 250°C for 24 h. These digests were then vacuum filtered, rinsed with 10% (v:v) nitric acid, and made to 20.0 mL volume with 10% nitric acid. These digested and filtered samples were then analyzed by flame atomic absorption using a Perkin-Elmer model 460 atomic absorption spectrophotometer, with deuterium arc background corrector (Perkin-Elmer 1976). Standard reference materials were analyzed concurrently with all samples to test for systematic errors in the digestion–analysis procedure. The details and results of the analyses of standard reference materials are given in Freedman (1978).

Analyses of total nitrogen and phosphorus in litter (previous section) were done using standard techniques described in Black *et al.* (1965) and Allen *et al.* (1974). Standard reference materials were analyzed concurrently to check for systematic errors in the procedure.

Observations and experimental results

Litter standing crop

The unit area standing crops of the 01 (litter) and 02 (duff) horizons were estimated at nine forested sites (Figs. 1A and 1B). Although within-site variation is high (maximum coefficient of variation for total 01 + 02 = 52%), there was a significant negative correlation between litter standing crop and distance from the smelter, i.e., the larger standing crops occurred close to the smelter (Fig. 1A). This higher standing crop cannot be accounted for solely by an accumulation of 01 litter relative to 02 duff (Fig. 1B).

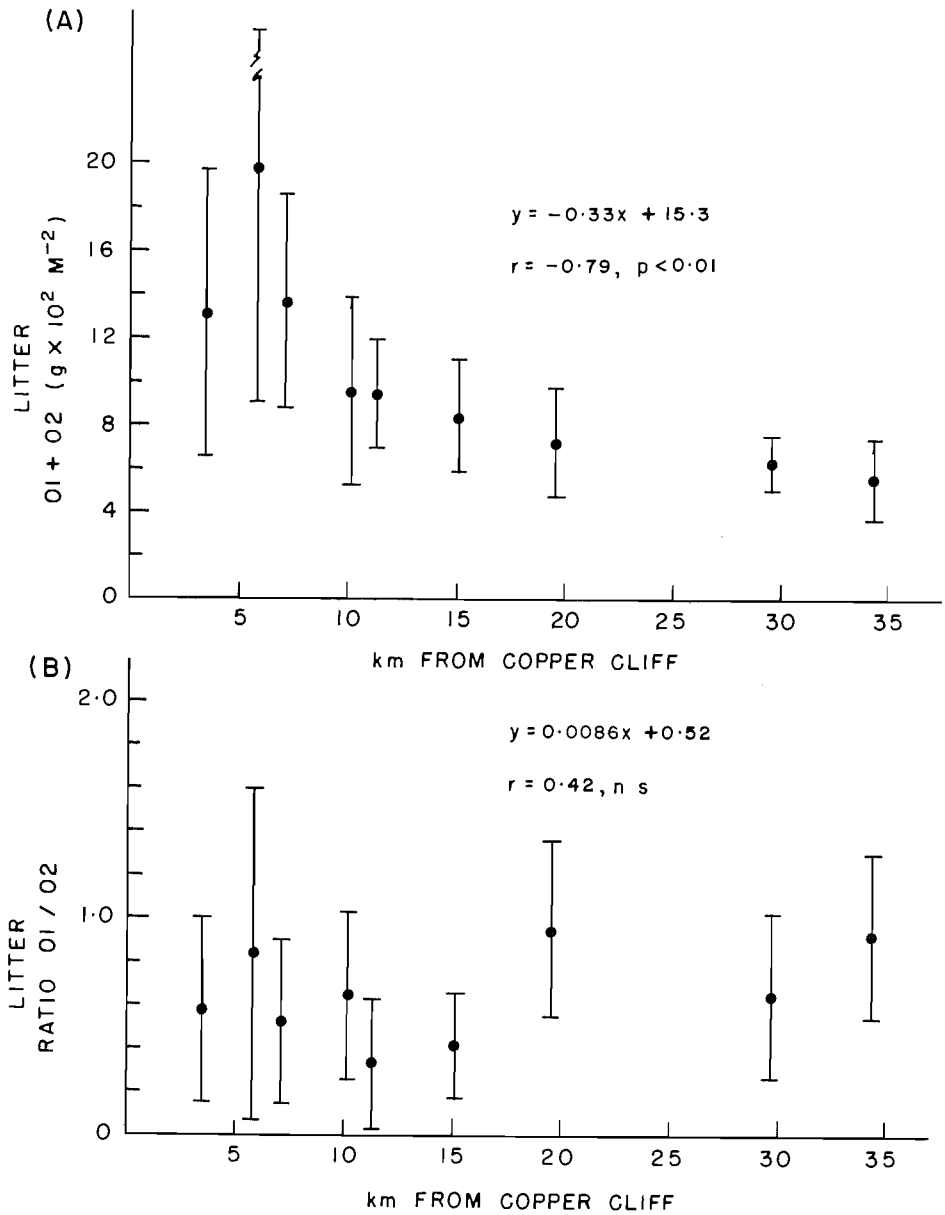

FIG. 1. (A) Total 01 plus 02 litter at forested sites; mean ±SD, *n* is equal to 15 replicate 0.25 m × 0.25 m quadrats per site. (B) Ratio of 01:02 standing crop; mean ±SD, *n* is equal to 15 replicates per site.

Litter accumulation ratio

The higher litter accumulation ratio observed at the two sites closest to the smelter (Table 1) is largely a function of their relatively higher 01 plus 02 standing crop, as little difference exists in litter fall between the sites close to and further away from Copper Cliff. The trend in litter fall was, in fact, to lower quantities at contaminated sites. Thus, decomposition appears to be retarded at the smelter-influenced sites.

Litterbag decomposition

Data for leaf litter decomposition rates are summarized in Table 2. The relative decomposition rates per species were *Betula papyrifera* > *Populus tremuloides* ≃ *Pinus strobus*. After the maximum exposure interval (851 days), weight loss for each species was greater at the two control sites than at the three contaminated sites, although these differences were not all statistically significant in the analysis of least significant difference (Table 2).

TABLE 1. Litter fall, litter standing crop, and the derived litter accumulation index for four forested sites south-southeast of the Copper Cliff smelter

Site distance, km	(A) Total leaf litter fall, g m^{-2} year^{-1}	(B) Total 01 + 02 litter, g m^{-2}	(B/A) Litter accumulation ratio
3.5	206±67	1310±660	6.4*
5.8	201±30	1980±1030	9.9*
29.7	259±27	620±130	2.4
34.3	223±37	550±180	2.5
	n = 6 quadrats (1 m × 1 m)	n = 15 quadrats (0.25 m × 0.25 m)	

*Significantly larger than 29.7- and 34.3-km sites at $p < 0.05$, t-test.

The relative rates of cation loss were potassium ≫ magnesium > calcium at the various sampling intervals (Table 3). Because there were no consistent site differences for any of the three species, representative data from only one site (34.3 km) are shown. Data from the other sites are in Freedman (1978). Loss of cations was markedly more rapid in the deciduous than in the coniferous species.

Decomposition of contaminated and control foliage

Data comparing decomposition rates of contaminated and control litter at a common site are summarized in Table 4. No significant differences were found in the weight loss between contaminated (i.e., relatively high copper and nickel content) foliage and that collected from the two control sites.

Soil CO_2 evolution measurements

The CO_2 evolution data for various transects and forest types are summarized in Tables 5 and 6. Although within-site variation was always high in these analyses (maximum coefficient of variation = 84%), on all sampling dates and for all transects there was a consistently lower rate of CO_2 flux from soil samples collected at sites closer to the smelter, relative to sites further away.

The data shown in Table 6 were collected in conjunction with assays of acid phosphatase activity and soil heavy metal (copper and nickel) analyses of subsamples of the same soil collections.

TABLE 2. Dry weight loss of leaves in 15-mesh litterbags placed at forest sites at various distances from the Copper Cliff smelter (mean percent loss ± SD)

Site distance, km	51 days	117 days	314 days	488 days	851 days
		Betula papyrifera			
3.5*	30±1	44±2	52±1	63±3	65±4
5.8*	28±2	43±2	51±5	57±3	62±8
8.0*	26±1	34±3	46±3	58±12	60±6
29.7†	40±4	51±1	61±6	67±10	68±3
34.3†	36±3	55±5	60±8	72±10	83±4
n	5	4	4	5	6
ANOVA significance	NS	0.01	0.01	0.01	0.05
$LSD_{0.05}$	—	5	5	7	8
		Populus tremuloides			
3.5*	15±0.4	26±0.7	35±2	39±3	41±3
5.8*	18±0.2	25±1	31±0.4	36±1	47±9
8.0*	20±1	25±1	32±1	36±2	39±8
29.7†	21±1	30±0.9	36±0.6	46±5	51±9
34.3†	22±0.8	28±2	39±2	47±2	53±4
n	5	4	4	5	6
ANOVA significance	0.01	NS	0.01	0.01	0.05
$LSD_{0.05}$	4	—	4	5	7
		Pinus strobus			
3.5*	11±0.2	17±0.4	32±0.5	40±2	44±9
5.8*	14±0.5	17±0.4	31±2	38±4	57±15
8.0*	20±0.5	24±2	35±2	40±0.7	50±2
29.7†	16±0.4	28±0.8	37±4	45±6	69±8
34.3†	13±0.1	20±0.5	32±0.5	50±4	58±9
n	5	4	4	5	6
ANOVA significance	0.01	0.01	NS	0.01	0.05
$LSD_{0.05}$	3	4	—	7	7

NOTE: NS, not significant.
*Contaminated forest sites.
†Control forest sites.

TABLE 3. Calcium, magnesium, and potassium loss from tree leaves confined in 15-mesh litterbags placed at a forested site 34.3 km south-southeast of the Copper Cliff smelter (mean percent loss ± SD)

	51 days	117 days	314 days	488 days
	Betula papyrifera			
Potassium	71±27	89±17	93±13	96±24
Magnesium	28±3	53±9	68±19	76±32
Calcium	37±4	33±6	34±8	52±7
n	5	4	4	5
	Populus tremuloides			
Potassium	73±22	86±12	90±27	94±31
Magnesium	24±3	38±6	65±11	64±9
Calcium	10±3	16±8	25±2	33±1
n	5	4	4	5
	Pinus strobus			
Potassium	9±1	37±1	71±12	88±14
Magnesium	9±3	18±1	43±8	73±14
Calcium	36±3	35±2	30±4	34±4
n	5	4	4	5

These data are described in more detail subsequently.

Soil acid phosphatase activity

Two separate collections of forest 02-A1 (duff-humus) samples were taken from sites at various distances from the smelter and assayed for acid phosphatase activity. The data from the second collection only are presented here (Table 6, Fig. 2). These samples were assayed for acid phosphatase activity and CO_2 flux, and then analyzed for total copper and nickel. Acid phosphatase activity at the denuded hilltop site was especially low. The data show differences in mean acid phosphatase activity between the three uncontaminated forest sites and the three sites closer to the smelter. However, not all of these differences were significant in the analysis of least significant difference (Fig. 2). The two most metal-contaminated forest sites, at 3.0 and 3.7 km, showed the lowest soil enzyme activities (Table 6). Differences in CO_2 flux also exist, although it is notable that the contaminated site located 5.2 km from the smelter exhibited mean rates comparable to those of one of the control sites. Soils from the denuded hilltop site at 3.0 km had much lower rates of both CO_2 flux and acid phosphatase activity than soils from a nearby forested site (Table 6).

Table 7 summarizes linear regressions and correlation coefficients which were calculated using the data from the June 2, 1977 experiment. All correlations presented are weak, but statistically significant. Total soil copper showed a stronger inverse relationship with both soil CO_2 flux and enzyme activity than did nickel. Copper plus nickel correlations gave intermediate values for both measurements of soil microbial activity. CO_2 flux and acid phosphatase activity were also significantly correlated.

Soil faunal collections

The soil faunal data (Table 8) were highly variable, with a maximum coefficient of variation of

TABLE 4. Dry weight loss of leaves collected from sites at various distances from the Copper Cliff smelter, and exposed in 15-mesh (0.17 cm screen size) litterbags at an uncontaminated forest site. Mean metal analyses of initial leaf material also indicated (mean percent loss ± SD)

Collection site	Distance, km	% dry weight loss		*n*	Initial copper, ppm	Initial nickel, ppm
		175 days	538 days			
		Alnus rugosa				
Kelley	3.4	45±4	59±9	3	94	207
Killarney	34.3	55±2	57±2	3	16	24
Hartley Bay	60.0	44±5	54±7	3	14	10
ANOVA significance		NS	NS			
		Acer rubrum				
Kelley	3.4	46±2	52±1	3	31	60
Killarney	34.3	48±1	56±3	3	9	5
Hartley Bay	60.0	50±2	59±8	3	11	4
ANOVA significance		NS	NS			
		Populus tremuloides				
Kelley	3.4	36±2	44±2	3	57	164
Killarney	34.3	38±1	46±2	3	12	37
Hartley Bay	60.0	40±1	46±1	3	8	17
ANOVA significance		NS	NS			

NOTE: NS, not significant.

TABLE 5. Summary of soil CO_2 evolution measurements from forested sites along the south-southeast transect (mean ± SD; 10 replicate determinations per site)

Site distance, km	CO_2 evolution	
	$\mu L\ CO_2\ min^{-1}\ core^{-1}$	$\mu L\ CO_2\ min^{-1} g^{-1}$ (g dry weight)$^{-1}$
Mesic *Populus tremuloides* forests: collected September 1975		
2.8	6±2	0.1±0.03
3.5	5±2	0.3±0.1
6.5	6±2	0.2±0.1
10.9	10±7	0.6±0.5
22.1	15±6	1.5±0.7
43.0	18±5	1.1±0.6
Mesic *Populus tremuloides* forests: collected June 1976		
1.6	5±1	0.1±0.05
3.0	5±1	0.2±0.1
7.4	18±6	1.8±0.5
15.0	17±4	1.1±0.7
28.7	15±3	0.4±0.1
42.4	15±4	0.4±0.1
Mesic mixed species forests on gentle slopes: collected June 1976		
3.5	6±3	0.2±0.1
5.8	9±3	0.7±0.5
10.2	13±6	0.9±0.6
19.0	16±5	0.9±0.5
29.7	26±6	1.8±0.7
34.3	17±4	1.8±0.6

200%. The July 17, 1976 data indicate significantly lower ($p < 0.01$) mite and springtail populations at the two contaminated sites relative to the two control sites. This pattern was not consistently found in July 14, 1976. However, this seems to be due to low population extraction at the 34.3-km site, since the other uncontaminated site, at 29.9 km, had significantly higher mite extractions than the contaminated sites, and than that of the 5.5-km site for Collembola.

Soil fungal populations

Soil fungal data are summarized in Table 9. Although within-site variation was quite high (maximum coefficient of variation = 109%), there were fewer numbers of colonies isolated from the contaminated site closest to the smelter, compared with the two control sites. However, an analysis of variance showed no significant differences. Populations at the other contaminated site were not consistently different from those of the two control sites. For all sites, most of the fungal colonies isolated were of the genus *Penicillium* (73% of total colonies), followed by *Trichoderma* (13%), *Mortierella* (10%), and *Mucor* (2%). Other genera isolated in low numbers (< 1%) include *Cladosporium*, *Aureobasidium*, *Phoma*, *Aspergillus*, *Discosia*, *Alternaria*, and *Verticillium*. It must be stressed, however, that not all soil fungi are equally selected for by the culture technique that was used, i.e., some groups (particularly prolific spore producers) are favoured over others (Black *et al.* 1972), and hyphae present in the soil may be missed or assigned low values.

Table 10 summarizes data on the effect of additions of copper and nickel, singly and in combination in the culture agar, on the numbers of fungal colonies isolated from soils from the contaminated and control forest sites. For all sites, the numbers of colonies isolated decreased with increasing concentrations of copper and nickel. In addition, the colonies that grew at the higher concentrations were relatively small compared with controls. The colony diameters at 100 ppm copper or nickel averaged about 10% of control colonies after the stan-

TABLE 6. Summary of acid phosphatase activity, CO_2 flux, and total metal analyses of 02-A1 (duff-humus) soil samples collected from sites at various distances south-southeast of the Copper Cliff smelter on June 2, 1977 (mean ± SD; n = 10 replicate collections per site)

Site distance, km	CO_2 flux		Enzyme activity		Total ppm dry weight	
	Rate per fresh weight	Rate per dry weight	Rate per fresh weight	Rate per dry weight	Copper	Nickel
3.0*	0.06±0.02	0.07±0.02	8.5±10.0	9.2±10.8	210±110	220±200
3.0†	0.18±0.09	0.26±0.14	41.6±16.2	63.9±19.3	2400±700	1400±400
3.7†	0.31±0.16	0.58±0.38	46.2±19.3	78.5±44.7	2600±800	1900±1400
5.2†	0.38±0.17	0.72±0.40	73.9±58.5	144.8±114.0	1400±400	1200±400
34.3‡	0.59±0.19	0.98±0.38	191.7±47.7	316.5±82.4	470±170	590±190
47.8‡	0.51±0.15	0.94±0.32	105.5±49.3	205.6±114.7	450±100	460±130
50.2‡	0.39±0.15	0.62±0.28	180.2±75.5	248.7±122.4	230±70	270±100

NOTE: CO_2 flux: microlitres CO_2 per minute per gram fresh weight or dry weight. Enzyme activity: micrograms *p*-nitrophenol produced per 20 min per gram fresh weight or dry weight.
*Devegetated hilltop. All other sites are forested.
†Contaminated forest sites.
‡Control forest sites.

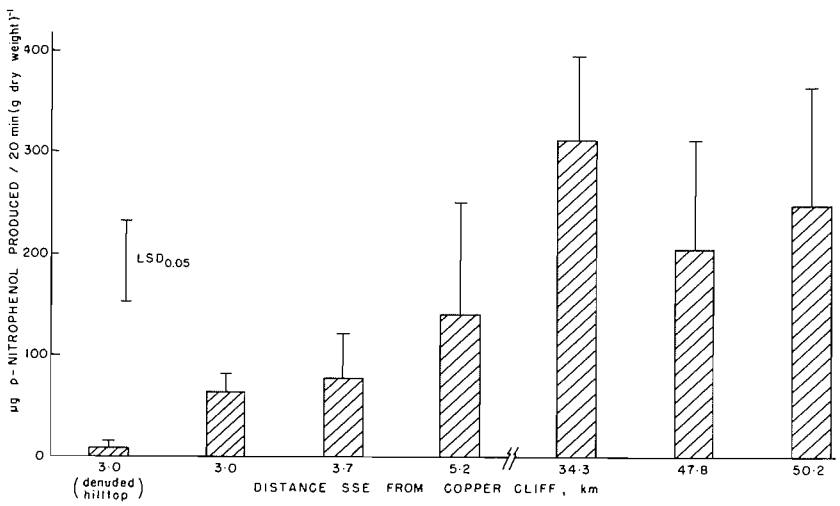

FIG. 2. Acid phosphatase activity of 02-A1 (duff-humus) soils from forest communities near Copper Cliff, Ontario; mean ± SD, n is equal to 10 replicate determinations per site.

TABLE 7. Linear regressions and correlation coefficients calculated using data from forested sites given in Table 8

(1) X = CO_2 flux (fresh weight)*	$Y = 216X + 18$
Y = phosphatase activity (fresh weight)†	$r = 0.48, p < 0.001, n = 60$
(2) X = CO_2 flux (dry weight)	$Y = 171X + 66$
Y = phosphatase activity (dry weight)	$r = 0.52, p < 0.001, n = 60$
(3) X = copper (ppm)	$Y = -0.000077X + 0.49$
Y = CO_2 flux (fresh weight)	$r = -0.41, p < 0.001, n = 60$
(4) X = nickel (ppm)	$Y = -0.000048X + 0.44$
Y = CO_2 flux (fresh weight)	$r = -0.21, p < 0.1, n = 60$
(5) X = copper + nickel (ppm)	$Y = -0.000038X + 0.48$
Y = CO_2 flux (fresh weight)	$r = -0.34, p < 0.01, n = 60$
(6) X = copper (ppm)	$Y = -0.044X + 162$
Y = phosphatase activity (fresh weight)	$r = -0.63, p < 0.001, n = 60$
(7) X = nickel (ppm)	$Y = -0.017X + 142$
Y = phosphatase activity (fresh weight)	$r = -0.40, p < 0.01, n = 60$
8) X = copper + nickel (ppm)	$Y = -0.023X + 159$
Y = phosphatase activity (fresh weight)	$r = -0.55, p < 0.001, n = 60$

*CO_2 flux: microlitres CO_2 evolved per minute per gram fresh weight or dry weight.
†Phosphatase activity: micrograms p-nitrophenol produced per 20 min per gram fresh weight or dry weight.

dard incubation period. At the highest concentration of copper used (100 ppm), the control site at 34.3 km showed a lower percent reduction in the number of colonies than did either of the two contaminated sites. However, at 100 ppm nickel both of the control sites produced fewer than 50% of the number of colonies isolated from either of the contaminated sites. When copper and nickel were added in combination to the medium, there was a greater reduction in the number of colonies than when the metals were added separately. At 100 ppm nickel plus 100 ppm copper the numbers of colonies were greatly reduced, but notably, all sites yielded colonies. With this treatment, no consistent differences were noted in the numbers of colonies isolated from the contaminated and control sites. For soils from all sites, the fungal genera isolated at the highest metal concentrations (i.e., > 100 ppm) were predominantly *Penicillium* (60% of total colonies), followed by *Trichoderma*, *Rhodotorula*, *Oidiodendron*, *Mortierella*, and *Mucor*.

Litter amendment experiment

The initial chemical characteristics of the litter used in this experiment are summarized in Table 11. The experimental data are summarized in Fig. 3

TABLE 8. Numbers of soil microarthropods extracted per core from forest soils collected at sites at various distances from the Copper Cliff smelter (mean ± SD; n = 60 replicate soil cores per site)

Site distance, km	*Collembola*	Mites	Others
Collection date: July 14, 1976			
3.5	1.9±2.3	1.1±1.3	0.3±0.6
5.5	1.1±1.3	2.4±2.8	0.4±0.7
29.9	2.1±2.3	3.3±3.4	0.8±1.1
34.3	1.3±1.9	2.2±2.5	0.5±0.7
ANOVA significance	0.05	0.01	NS
$LSD_{0.05}$	0.7	0.6	—
Collection date: July 17, 1976			
3.5	1.5±1.9	2.5±2.1	0.4±0.7
5.5	1.3±1.5	3.3±3.1	0.5±0.7
29.9	2.7±2.5	5.1±3.8	0.6±0.7
34.3	4.4±4.1	5.0±3.5	0.8±1.5
ANOVA significance	0.01	0.01	NS
$LSD_{0.05}$	1.0	1.2	—

NOTE: NS, not significant.

TABLE 9. Total fungal colonies (soil dilution method, Rose-Bengall agar) isolated from forest soils collected in 1976 from two contaminated and two control sites near Sudbury, Ontario

Site distance, km	Total no. of fungal colonies isolated ($\times 10^5$/g fresh weight soil)		
	June 7	July 1	July 8
3.5	1.4±0.5	1.1±0.3	1.8±0.5
5.8	4.3±4.7	2.6±1.3	3.3±0.7
29.7	1.9±1.1	2.7±2.9	4.1±2.6
34.3	4.0±1.9	2.5±1.4	3.7±1.8
n (samples per site)	5	4	4
ANOVA significance	NS	NS	NS

NOTE: NS, not significant.

(relative weight loss) and Fig. 4 (relative CO_2 flux at the end of the experiment). The data in Fig. 3 indicate that copper and (or) nickel retard the decomposition of litter under controlled conditions. Both copper and nickel inhibit decomposition when they are present in the litter in concentrations of 1000 ppm or more. Copper exerts a more negative effect than nickel at the same concentration. The relative difference is maintained when the copper–nickel comparisons are made on a molar basis (relative atomic weights copper–nickel = 1.082). When copper and nickel are present together in concentrations of 500 ppm, they exert an inhibitory effect on decomposition, even though separately they had no effect at 500 ppm (Fig. 3). At higher concentrations of both metals together, only small increases in inhibition were noted over the effects of single metals.

The data for CO_2 flux, measured at the end of the 60-day incubation period, are summarized in Fig. 4. These data are much more variable than the data for relative litter weight loss (coefficient of variation of control = 37%, versus 3% for weight loss). In spite of this inherent variation, the data suggest that copper and (or) nickel in litter depresses the rate of CO_2 evolution. At most metal concentrations, copper exerts a stronger inhibition than nickel. When both metals are present together, the effect is much greater than that observed when the metals are present separately.

Discussion

The evidence presented indicates a trend towards an increased accumulation of litter at sites closer to the Copper Cliff smelter (Fig. 1A). This litter is not especially accumulating as 01 (litter) relative to 02 (duff) (Fig. 1B), as was found by Watson *et al.* (1976), who considered this observation to be evidence of decreased 01 mineralization due to high levels of heavy metals (mainly lead and zinc) in soils near a primary lead smelter. In the present study, the accumulation of 01 and 02 litter at the contaminated sites appears to be due to decreased rates of decomposition, since the differences in the calculated litter accumulation ratio between the contaminated and the control forest sites are due to differences in litter standing crop, and not to differences in total leaf litter fall (Table 1). Accumulation of litter in forests near various smelters has previously been noted (Watson 1975; Watson *et al.* 1976; Jordan and Lechevalier 1975; Martin 1977; Strojan 1978*a*; Coughtrey *et al.* 1979). Strojan (1978*a*) related litter accumulation to relative rates of litter input. He found only a slight reduction in litter input at his contaminated site, and concluded that the observed differences in litter standing crop were due to decreased litter decomposition. This parallels our observations at the Sudbury sites. His sites were contaminated by lead, zinc, and cadmium, whereas ours are contaminated by nickel and copper especially.

Litterbag studies showed that the leaf weight loss of each of the three species was greater at the control sites than at the contaminated sites after 851 days (Table 2), although not all of the differences between the three contaminated and the two control sites were significant. Strojan (1978*a*) found leaf litter weight losses at a contaminated smelter site (up to 26 000 ppm zinc, 2300 ppm lead, 900 ppm cadmium in 02 litter) to be only about half of that observed at a control site.

The relative decomposition rates in our study were *Betula papyrifera* > *Populus tremuloides* ≃ *Pinus strobus* (Table 2). In leaf decomposition

TABLE 10. The effect of copper and (or) nickel in Rose–Bengall agar on the number of microfungal colonies isolated from mesic forest soils collected at various distances from smelter

Treatment	3.5-km site		5.8-km site		29.7-km site		34.3-km site	
	colonies $\times 10^4$	%	colonies $\times 10^4$	%	colonies $\times 10^4$	%	colonies $\times 10^4$	%
Control	18.3±4.6	100	33.2±6.9	100	40.9±25.7	100	36.6±17.9	100
25 ppm copper	13.0±5.7	71	24.2±3.7	73	33.3±28.2	81	31.0±15.4	85
50 ppm copper	8.0±2.9	44	15.1±9.7	45	18.1±14.7	44	24.1±15.5	66
100 ppm copper	8.0±3.3	44	12.6±10.1	38	10.0±6.2	24	20.9±16.0	57
25 ppm nickel	13.9±5.7	76	25.2±7.2	76	30.8±22.0	75	22.8±12.2	62
50 ppm nickel	12.4±3.5	68	23.1±9.3	70	20.3±19.6	50	14.6±11.3	40
100 ppm nickel	9.6±3.4	52	16.1±5.5	49	8.9±4.1	22	5.8±5.6	16
50 ppm Cu + 50 ppm Ni	5.2±1.8	28	15.3±11.9	46	7.3±4.9	18	6.8±6.1	19
100 ppm Cu + 100 ppm Ni	2.1±1.4	11	1.2±0.3	4	1.4±1.3	3	0.8±0.3	2

TABLE 11. Initial chemical characteristics of litter used in a copper–nickel perturbation experiment

Characteristic	Mean concentration ± SD	No. of replicates analyzed
Copper	210±30 ppm	5
Nickel	70±10 ppm	5
Zinc	160±20 ppm	5
Iron	3400±400 ppm	5
Phosphorus	620±20 ppm	4
Nitrogen	1.2±2%	4
pH	4.6 (range 4.4–4.7)	6

studies under controlled laboratory conditions, Daubenmire and Prusso (1963) found relative decomposition rates to be *Populus tremuloides* > *Betula papyrifera* > *Pinus* spp. at 10°C, and *Betula papyrifera* ≃ *Populus tremuloides* > *Pinus* spp. at 25°C. Broadfoot and Pierre (1939) found the decomposition rates of homogenized leaf tissue of *Pinus* spp. to be less than those of most angiosperm tree species when examined under controlled conditions. It is generally held that coniferous leaf litter is relatively resistant to decomposition compared with broadleaf angiosperm litter (Millar 1974).

Relative net losses of calcium, magnesium, and potassium from leaf litter were also examined (Table 3). None of the three tree species showed consistent differences between the two control sites and the three contaminated sites closer to the smelter. The relative rates of loss were potassium ≫ magnesium > calcium at the various sampling intervals. This trend agrees with the observations of Attiwill (1968), Gosz *et al.* (1973), and Strojan (1978*a*). These authors found that potassium, and to a lesser extent magnesium, were rapidly lost from litter by leaching, but that calcium release was similar to weight loss, indicating that calcium behaved as a structural component that was primarily lost by decomposition. Similar conclusions can be drawn from this study, although magnesium appears to be lost more slowly, compared with these other studies. *Pinus strobus* strongly retained calcium after the initial 51-day period.

No significant differences were found in rates of decomposition that could be related to the different initial copper or nickel contents of the foliage when exposed at uncontaminated forest sites (Table 4). This indicates that initial substrate differences may be less important than site differences with respect to effects on litter breakdown (cf. Table 2). Strojan (1978*a*) made similar observations when he compared the relative rates of decomposition of contaminated and control leaves of *Sassafras albidum* and *Quercus* spp. collected at sites near a zinc smelter near Palmerton, Pennsylvania.

On all sampling dates there were consistently lower rates of CO_2 flux from soil samples collected at sites closer to the smelter, relative to sites further away (Tables 5 and 6). The lower rates of CO_2 flux at the contaminated sites may be related to decreased soil microbial activity. The CO_2 flux at the most contaminated forest sites were especially low (e.g. 3-km forest site in Table 6). Other studies have measured CO_2 flux from smelter-polluted soils as an index of relative soil respiration, and have made similar observations. In a series of papers investigating a brass foundry at Gusum, Sweden, contaminated over a period of 300 years with copper, zinc, and various other heavy metals, Rühling and Tyler (1973), Tyler (1974, 1975*a*, 1976*a*), and Ebregt and Boldewijn (1977) noted decreased CO_2 flux from contaminated spruce needle mor soils relative to uncontaminated soils. These effects were correlated with soil heavy metal burdens.

The assay of soil acid phosphatase activity is considered here to be an index of overall soil respiratory activity. The technique used gives an approximation of extracellular activity, plus an un-

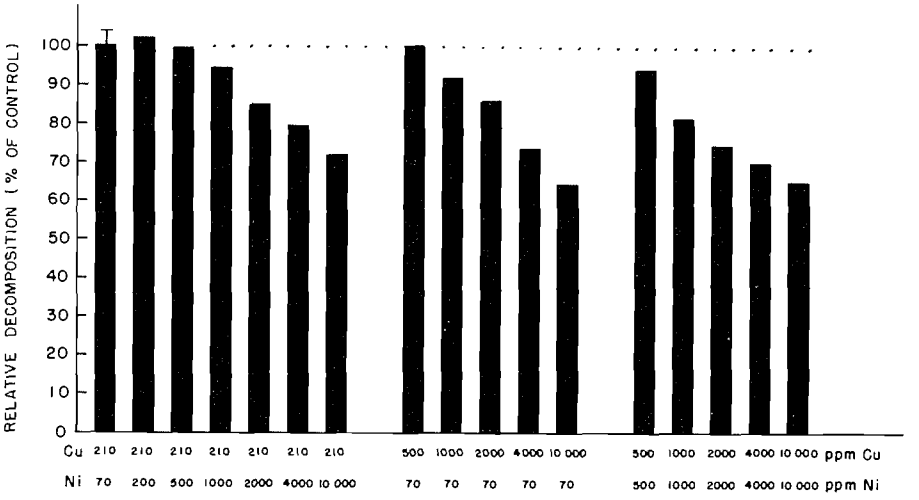

FIG. 3. Relative decomposition after a 60-day incubation of control litter, and litter amended with various concentrations of copper and (or) nickel. Control, mean ± SD, *n* is equal to six replicates. All other determinations, mean, *n* is equal to two replicates.

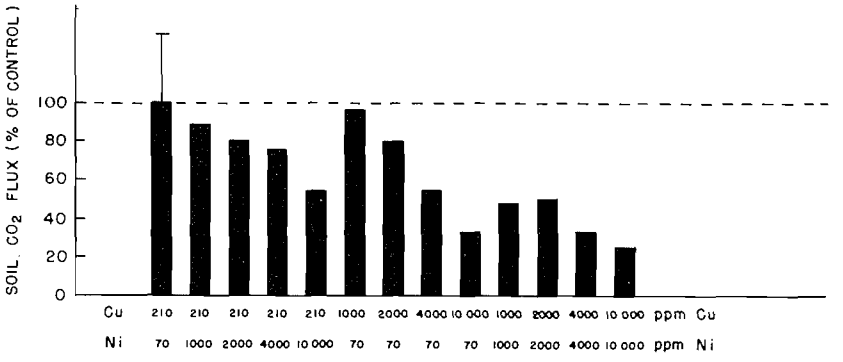

FIG. 4. Relative CO_2 flux from litter after a 60-day incubation of control litter, and litter amended with various concentrations of copper and (or) nickel. Control, mean ± SD, *n* is equal to six replicates. All other determinations, mean, *n* is equal to two replicates.

known fraction of the total intracellular acid phosphatase activity (Skujins 1976). Acid phosphatases are important soil enzymes, since assimilation of phosphate from organic compounds (30 to 70% of the total soil phosphate is organically bound), by both higher plants and microorganisms, is preceded by hydrolysis of the bound phosphate by extracellular phosphatase enzymes (Skujins 1976).

The data for two separate soil collections and assays indicate a large decrease in acid phosphatase activity in contaminated sites close to the smelter, relative to control sites (Table 6, Fig. 2). The sites most contaminated with nickel and copper showed the least activity (Table 6).

The CO_2 flux from aliquots of the same soil samples analyzed for acid phosphatase activity in the June 2, 1977 experiment was also measured. A general correlation with distance from the smelter existed, although the control site at 50.2 km was exceptional, having a relatively low CO_2 flux compared with the other uncontaminated sites (Table 6). Soils from a devegetated mineral-soiled hilltop close to the smelter had much lower rates of both CO_2 flux and acid phosphatase activity than soils from a nearby forested site (Table 6).

When the relationship between the concentration of copper or nickel in the soils with the evolution of CO_2 and the activity of acid phosphatase was examined, using correlation coefficients (Table 7), it was shown that correlations with copper accounted for much more of the variation than did nickel. This can be interpreted to mean that the pollution by copper is having a greater influence on litter decomposition and on acid phosphatase activity than equal amounts of nickel. Additional support for this hypothesis is given by the experi-

ment in which litter was amended with nickel and copper and then incubated under controlled laboratory conditions. Here (Figs. 3 and 4), it was found that copper had a greater effect in inhibiting weight loss and CO_2 evolution. Additional support is found in the literature. Horsfall (1956) found that copper had a more potent fungicidal effect than nickel in a series of laboratory experiments. On the other hand, Bhuiya and Cornfield (1972) and Cornfield (1977), studying the effects of additions of various metals to soils on subsequent rates of CO_2 evolution, found that nickel had a slightly more inhibitory effect than copper.

Similar observations have been made by other authors who have investigated the effects of heavy metal pollution of forest soils near smelters on soil acid phosphatase activity. Tyler (1974, 1975*a*, 1976*a*) found lower soil acid phosphatase activity at sites contaminated with copper and zinc, relative to uncontaminated sites, at a smelter at Gusum, Sweden. He noted (Tyler 1974) that it was unclear whether the decreased enzyme activity in the metal-polluted soil was due to (*i*) lower enzyme concentrations in the soil, or (*ii*) inactivation of soil enzymes by heavy metals. These two possibilities also apply to the present study. Tyler used a multivariate analysis to show that copper accounted for most of the observed enzyme inhibition. In the present study the soil contamination differs from that at Gusum, but includes copper. Mather and Rayment (1977) studied the effects of copper additions in the laboratory to organic agricultural soils. They found significant decreases in acid phosphatase activity when soils had a concentration of 5000 ppm of copper added, and ascribed this to an inactivation of extracellular phosphatase enzymes. In another laboratory experiment, Juma and Tabatabai (1977) looked at the effects of various concentrations of 20 separate trace metals on soil phosphatase activity. These authors noted decreases in activity following addition of copper and nickel, and noted that copper had approximately twice the inhibitory effect of nickel. Tyler (1976*b*) also found decreased acid phosphatase activity in soils amended with various concentrations of vanadium (up to 100 ppm) in a controlled, laboratory experiment.

Other soil enzymes have also been assayed with respect to the effect of heavy metal-polluted soils near smelters. At the Gusum site already mentioned, Rühling and Tyler (1973) noted a decrease in dehydrogenase activity in the copper- and zinc-contaminated soils close to the smelter. At the same site, Tyler (1974, 1975*a*) found decreased urease activity in the contaminated soils, but no effect on β-glucosidase. Also at Gusum, Ebregt and Boldewijn (1977) found decreased starch amylase activity in the contaminated soils. Finally, at a mine waste site in Wales contaminated by lead and zinc, Williams *et al.* (1977) found decreased urease activity in contaminated soils, relative to controls.

The July 17, 1976 data for soil faunal populations (Table 8) indicate significantly lower mite and springtail populations at the two contaminated sites relative to the two control forest sites. This pattern was not, however, found in the July 14, 1976 data. More concrete conclusions relevant to the effects on the soil fauna of litter contamination by smelter-derived pollutants at Sudbury await more detailed studies, particularly of species composition relative to control sites, but certainly it is apparent that some of the soil fauna can tolerate the metal-contaminated forest soils close to the smelter.

Watson (1975) and Watson *et al.* (1976) investigated the impact of a metal-contaminated (mainly lead and zinc) site near a lead smelter in Missouri on soil arthropods. They found that reduced values of arthropod density, diversity, richness, and biomass occurred simultaneously with elevated concentrations of heavy metals in litter at sites closer to the smelter. Lead, zinc, copper, and cadmium were found in elevated concentrations in soil arthropods from contaminated sites, and predatory mites were found to concentrate lead, zinc, and cadmium relative to detritivore or fungivore prey species. These authors also found large spatial variation in their arthropod collections, with a maximum coefficient of variation of 330% being observed for density data collected from the 01 litter horizon, and 67% from the 02 duff horizon. They felt that this high variation was due to physical soil factors, such as temperature or relative humidity. In another study, Strojan (1978*a*, 1978*b*) found lower numbers and diversity of arthropods inhabiting forest litter at metal-contaminated sites close to a smelter near Palmerton, Pennsylvania, compared with uncontaminated control sites.

There were consistently lower numbers of soil fungal colonies isolated from the 3.5-km contaminated site, relative to the other sites investigated in this study (Table 9). However, none of these differences were significant in an analysis of variance. This may be partly due to the low number of spatial replicates used in the study. Populations at the other contaminated site examined (5.8 km) were not consistently different from those of the two control sites. Carter (1978) also looked at fungal populations isolated from similar soil samples collected in November 1976 from the same forest sites

investigated in this study. He noted high spatial variation in his population estimates, and also found no statistically significant differences in fungal populations between contaminated and control sites when his data were expressed on a soil fresh weight basis. However, when his data were expressed on a soil dry weight basis, significant decreases in the fungal populations at the contaminated sites relative to the controls were calculated in the analysis of variance. He found four species of fungus that were present only at the contaminated sites at 3.5 and 5.8 km from the smelter, and not at either of the uncontaminated sites at 29.7 and 34.3 km. The most conspicuous isolate confined to the contaminated soils was *Penicillium waksmanii*, which made up 17 and 25% of the total isolates from the 3.5- and 5.8-km sites, respectively.

Other studies have looked at the effects of metal-polluted soils near smelters on microbial populations. Jordan and Lechevalier (1975) found decreased numbers of fungi, actinomycetes, and bacteria in contaminated soils close to the Palmerton zinc smelter in Pennsylvania. Hartman (1976) looked at fungi in soils contaminated with cadmium, copper, lead, and zinc near the Anaconda smelter in Montana, and found decreases in fungal populations and species diversity. Williams *et al.* (1977) found reduced fungal populations in both soils and litter near a Welsh lead–zinc smelter site. At sites near the Avonmouth smelter in England contaminated with zinc, lead, and cadmium, Gingell *et al.* (1976) and Martin (1977) found decreased numbers of soil fungi, bacteria, and yeasts, and also noted low numbers of phylloplane fungi.

When the numbers of fungal isolates and their growth rates were determined on agars amended with a range of copper and (or) nickel concentrations, it was found that the numbers of colonies isolated decreased with increasing concentrations of the metals (Table 10). In addition, the colony diameters were relatively small at the higher metal concentrations, indicating slower mycelial growth rates. Notably, copper- and nickel-tolerant fungi were isolated from both contaminated and control forest sites (i.e. they could grow at high metal concentrations in the agar). Carter (1978) also isolated fungi on an agar amended with nickel from soils collected from the same forested sites as ours, and made similar observations to those described above. Fungi preadapted to soils contaminated with nickel and copper are not uncommon in uncontaminated soils of the Sudbury area.

Jordan and Lechevalier (1975) found a decrease in the numbers and growth rates of fungal colonies isolated from soils when the nutrient agars were amended by adding various concentrations of zinc. They also isolated zinc-tolerant fungi from uncontaminated sites, and little difference was seen in the relative levels of zinc tolerance of fungi between the contaminated and control forest soils. They made similar observations for actinomycetes and bacteria. Hartman (1976) compared colonies of *Fusarium oxysporum* isolated from contaminated and control soils in his area with respect to tolerance to these metals in the growth medium, and found the smelter populations to be relatively tolerant, although both "ecotypes" were capable of growth in the presence of the metals. He noted that concentrations of metals in the mycelium reached very high levels, with up to 18 150 ppm dry weight copper, 14 300 ppm cadmium, 29 000 ppm zinc, and 132 000 ppm lead.

The decomposition of litter incubated under controlled laboratory conditions was retarded by the presence of both copper and nickel (Fig. 3). Both metals begin to exert a negative effect when present in concentrations of 1000 ppm. Such total metal concentrations in litter are frequently observed within 15 km of the Copper Cliff smelter (Freedman and Hutchinson 1980*a*). When copper and nickel are each present in the litter in concentrations of 500 ppm, they together exert a negative effect on mineralization, even though separately they had no effect at 500 ppm. This indicates a possible more than additive effect of the two metals, i.e. synergism. At higher concentrations of the two metals together, the inhibitory effect was only slightly more than when the metals were present separately.

Additions of copper and (or) nickel also depressed the rate of CO_2 evolution from the litter (Fig. 4). These flux data are much more variable than the data for litter mineralization (coefficient of variation of control = 37%, versus 3% for weight loss). This may be partially due to the instantaneous nature of the CO_2 flux measurements, which are subject to the effects of short-term variation in water content, temperature, etc., whereas the mineralization measurement is time integrating, so that the short-term variations are inconsequential. At most metal concentrations, a depression of CO_2 flux was measured relative to the control litter. When both metals were present together, the effect was much greater than that observed when the metals were present separately.

As already referred to, copper was more inhibitory than nickel to both litter mineralization and CO_2 evolution. This agrees with the observations of Horsfall (1956), who found copper to be a more potent fungicide than nickel, and of Juma and

Tabatabai (1977), who noted increased copper inhibition compared with nickel on soil acid phosphatase activity. Similarly, Bhuiya and Cornfield (1972) and Cornfield (1977) described the effects of separate additions of 12 metals on CO_2 flux from a sandy soil. They observed large reductions following copper and nickel additions (although nickel was slightly more inhibiting than copper in their experiments), and made similar observations for most of the other metals examined.

In summary, elevated concentrations of smelter-derived heavy metal and sulfur pollutants in soils and vegetation near the large Sudbury area smelters have been previously reported. The implications of the greatly increased heavy metal burdens on rates of litter decomposition on the forest floor have been investigated in the present study. Litter standing crops relative to rates of litter input are high at sites closer to the smelter, indicating that an accumulation of litter is occurring. This is reflected in a trend to relatively low rates of litter decomposition in litterbags placed at contaminated forest sites closer to the smelter, relative to control sites. No differences were seen, however, in the rate of decomposition of leaf litter contaminated with copper and nickel, relative to uncontaminated leaves of the same species. Certain activity indices related to litter decomposition (i.e. soil acid phosphatase activity and soil CO_2 flux) also indicate trends to lower rates at contaminated forest sites relative to control sites, although not all of the site differences were statistically significant. Both CO_2 flux and soil acid phosphatase activity were negatively correlated with copper and nickel concentrations in the soil. As well, rates of litter decomposition and CO_2 flux have been shown to be depressed by additions of various concentrations of nickel and (or) copper in a laboratory experiment, confirming that high concentrations of these metals will depress the mineralization of litter. Copper had a more inhibitory effect than nickel at equal concentrations.

At the levels of pollutant concentrations which presently exist at contaminated forested sites close to the Copper Cliff smelter, various independant measures related to rates of litter breakdown in forest soils indicate trends to lower rates relative to uncontaminated forest sites. However, litter breakdown still occurs even at the most contaminated forested sites, indicating a slowing down, but not an elimination of nutrient cycling within the stands. This phenomenon is an aspect of the effects of smelter pollution on surrounding plant communities which must be considered when assessing the environmental impact of such industrial developments. However, it must be stressed that the short-term effects of this slowing of mineral cycling on plant communities are small relative to those due to frequent and intense fumigations by sulfur dioxide or sulfuric acid mists, or soil toxicity to higher plants due to acidity or heavy metal burdens in soils. Key questions in the longer term are whether the decomposer microflora and fauna can fully adapt to the concentrations of metals present, whether the metals will continue to accumulate, and whether acid inputs might increase metal solubility and, therefore, toxicity to litter decomposers.

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